

# Natural Resource Damage Assessment: Fate and Effects of Dispersed Oil

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### Why Consider Dispersants?

- Aerial application of dispersants can mitigate large amounts of oil if treated promptly.
  - Mitigate -- reduce the overall impact of an oil spill to the environment as a whole.
  - However, dispersant use is a trade-off with increased risks to the water column balanced against reduced injury to surface water and shoreline resources.





### How do dispersants work?

 The function of dispersants is to reduce the oilwater interfacial surface tension and thereby greatly enhance the transfer of oil droplets from the water surface into the water column, as shown in the following equation.

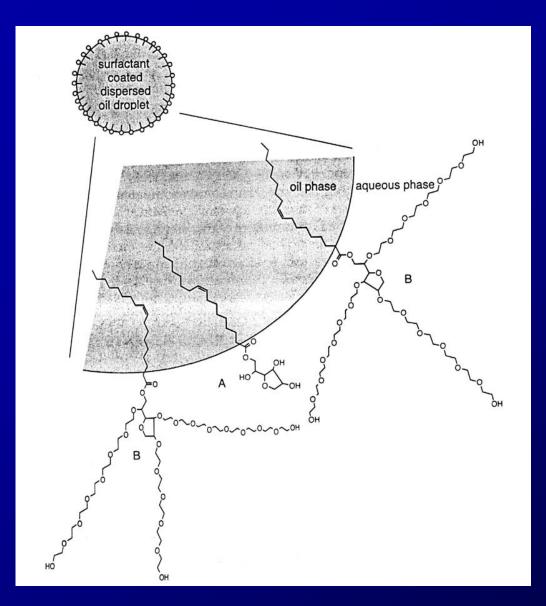
$$W_K = \gamma_{o/w} A_{o/w}$$

Where:

 $W_{K}$  = mixing energy  $\gamma_{O/W}$  = oil-water interfacial surface tension, and  $A_{O/W}$  = oil-water interfacial surface area.

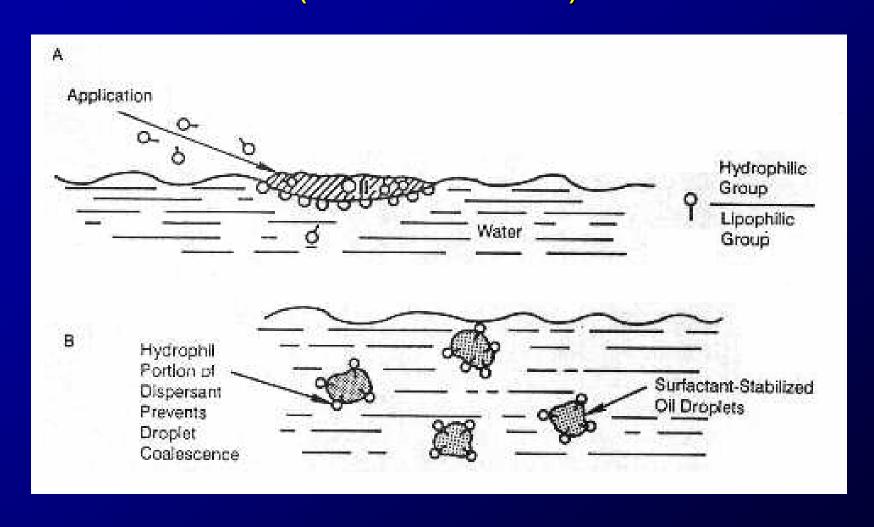
# Just Like Dawn® Dish Washing Detergent?

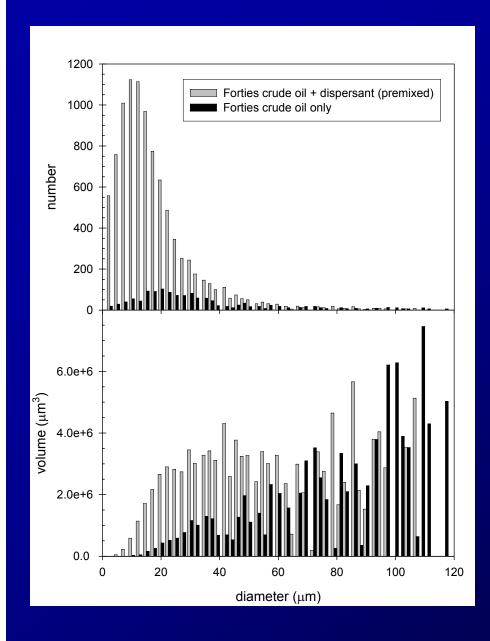
- Dispersants are surfactants dissolved in a solvent. Surfactants reduce the interfacial tension between water and oil, permitting the oil to break into tiny droplets with less energy required.
- Dispersants enhance a natural process.
- The ultimate fate of oil spilled in the marine environment is biodegradation. Dispersion enhances the rate of natural biodegradation by significantly increasing the surface-area-to-volume ratio of the spilled oil.



Orientation of Surfactants at Oil-Water Interface (from NRC 2005)

### Mechanism of Chemical Dispersion (from NRC 1989)





Oil droplet size distribution (in µm) of premixed Forties crude oil and Slickgone NS measured at sea using a Phase Doppler Particle Analyzer (from Lunel 1995b and NRC 2005).

### Dispersant Use in California

#### **PAST:**

- Quick-approval process (RRT)
- Hesitation to use dispersants
- Concerns about effectiveness and impacts
- Limited equipment and supplies





### Dispersant Use in California

#### **NOW:**

- Pre-approval zones
- Quick-approval zones (through RRT)
- California Dispersant Plan
- Equipment & supplies
- Education
- Acceptance of dispersants
- SMART



Future use of dispersants in CA likely

# Scientific Monitoring of Advanced Response Technologies (SMART): A Tiered Program

- Tier I employs the simplest operation, visual monitoring.
- Tier II combines visual monitoring with onsite fluorometry at a single depth with watersamples collected for later analysis.
- Tier III advanced Tier II.

#### **SMART**

Special Monitoring of Applied Response Technologies (SMART)

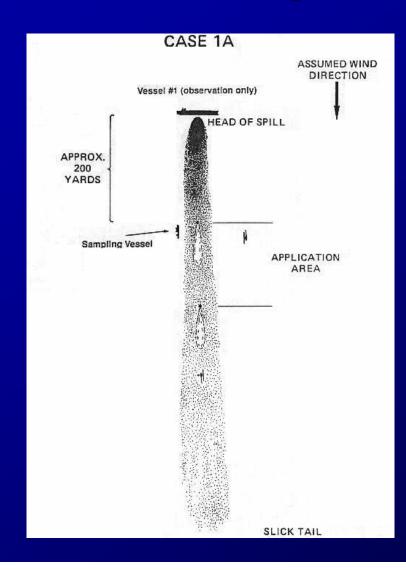
SMART measures
 effectiveness of dispersant
 application to assist
 Incident Commander

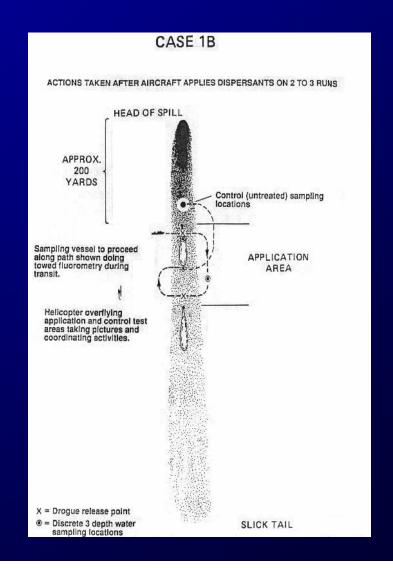
 SMART does not measure effects of dispersed oil on wildlife or exposed organisms



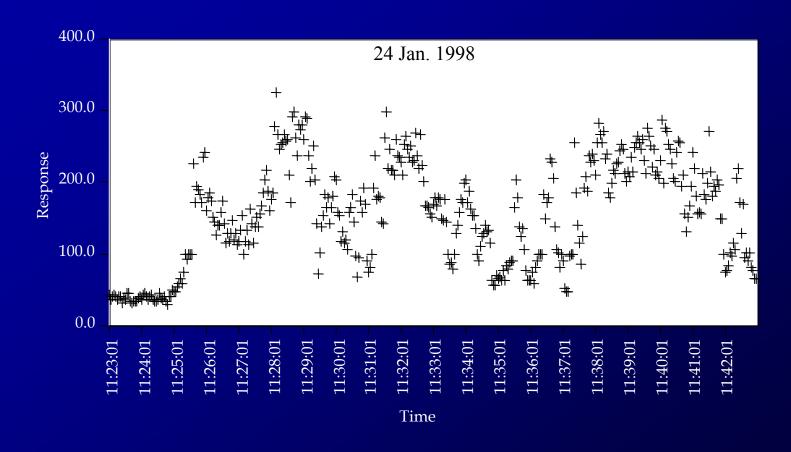


# Approaches to Effectiveness Monitoring (from Payne et al. 1991)



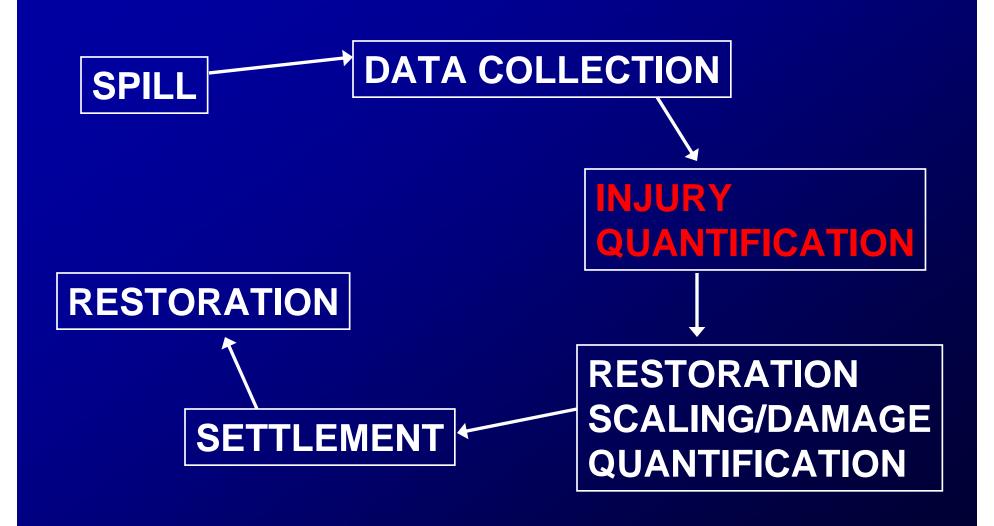


### Tier II SMART Data: HIPS



Note the "patchy" nature of a dispersed oil plume.

### NRDA Process:



# California Dispersed Oil Monitoring Plan (DOMP)

#### Principle investigators:

- R. Lewis
- Dr. W. Nordhausen
- Dr. D. French McCay
- Dr. J. Payne

#### Collaborators:

- Y. Addassi
- M. Sowby
- Dr. J. Cubit
- H. Parker Hall







# California Dispersed Oil Monitoring Plan (DOMP)

### **Objectives**

- Develop a plan to quantify and evaluate impacts to aquatic organisms after a spill where dispersants are used
- Provide data for NRDA
- Evaluate effects for decision making for future spills

### Dispersed Oil Monitoring Plan

### HOW?

- Quantity (size of dispersed oil plume)
- Components (dissolved-phase & oil droplets)
- Concentration
- Duration
- Environmental impact
- Documentation

→ Sampling plan

# Dispersed Oil Monitoring Plan Our approach...

- Computer simulation using ASA's
   Spill Impact Model Application Package (SIMAP)
   combined with Biological Exposure Model
- Prepare sampling plan based on simulation results
- Prepare standby equipment & retain contractors





# SIMAP 3D Transport and Fates Model

- Surface slicks
- Subsurface droplets
- Water column aromatics: dissolved and oil phase
- Sediment aromatics: dissolved and adsorbed
- Sediment total hydrocarbons
- Response module
- Shoreline deposition and removal
- Mass balance

### SIMAP Modeling Matrix

- Hypothetical spills in open water.
- Oil type: Light Arabian crude.
- Spill volume: maximum volume of oil dispersed by a single sortie of a C-130 (5,000 gallons dispersant at 1:20 DOR = 100,000 gallons treated). An assumed 80% efficiency yields 80,000 gal of dispersed oil.
- Oil thickness: median value for dispersant application (100 µm).
- 3 dispersant application scenarios: none; after weathering 8 hrs, after weathering 16 hrs.
- 2 wind speeds and associated turbulence conditions: 5 kts,
   15 kts.
- Restricted to surface mixed layer: 10m or 20m.
- Background currents: none, 0.25 kts downwind, 0.25 kts upwind.

#### **Scenario**

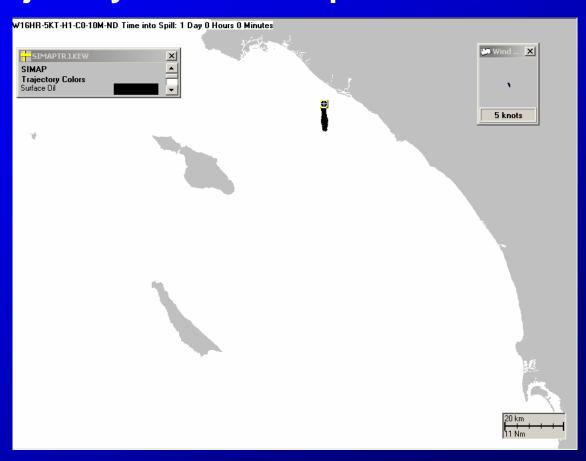
**Pre-Weathering for 16 hrs before potential treatment** 

Wind from NNW 5 kts; Currents: 0 kt;

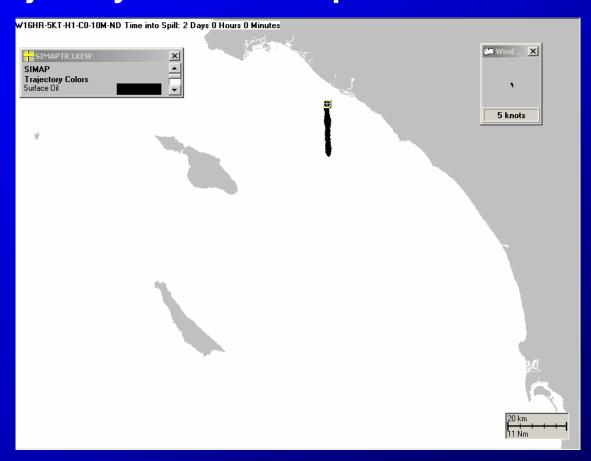
**Dispersant: none** 

**Turbulent Mixing to 10m deep in Surface Mixed Layer** 

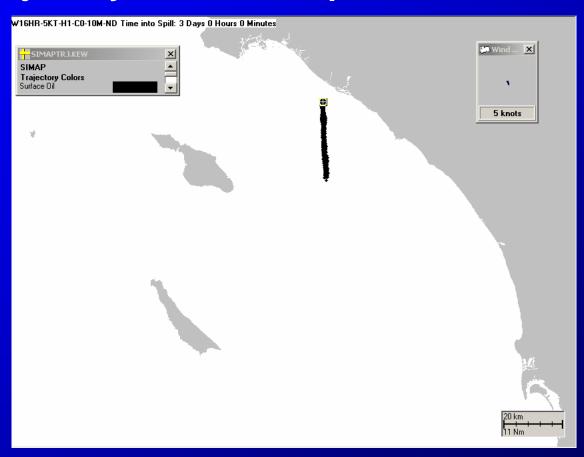
Trajectory: 24 hrs after potential treatment



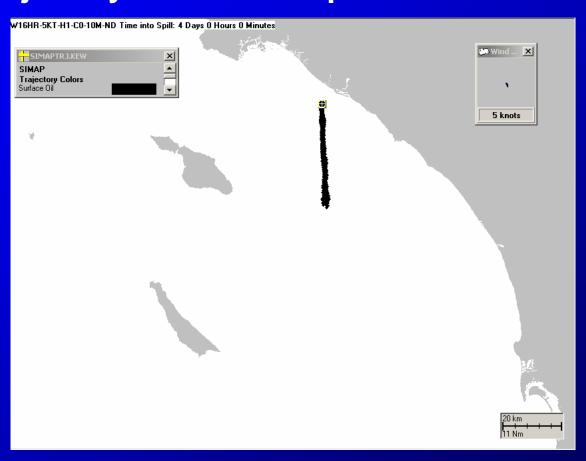
Trajectory: 48 hrs after potential treatment



**Trajectory: 72 hrs after potential treatment** 

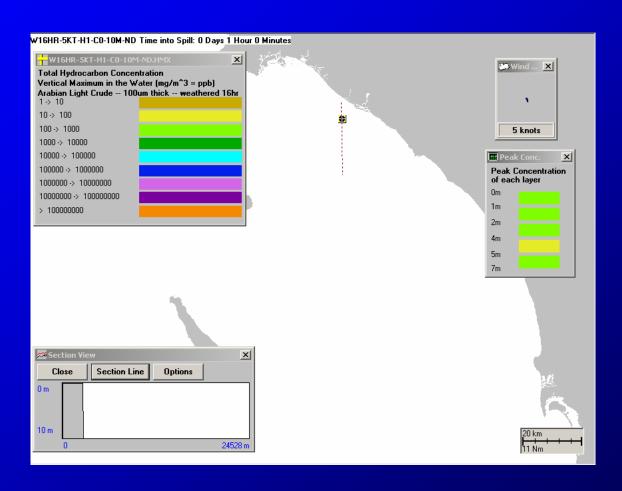


Trajectory: 96 hrs after potential treatment

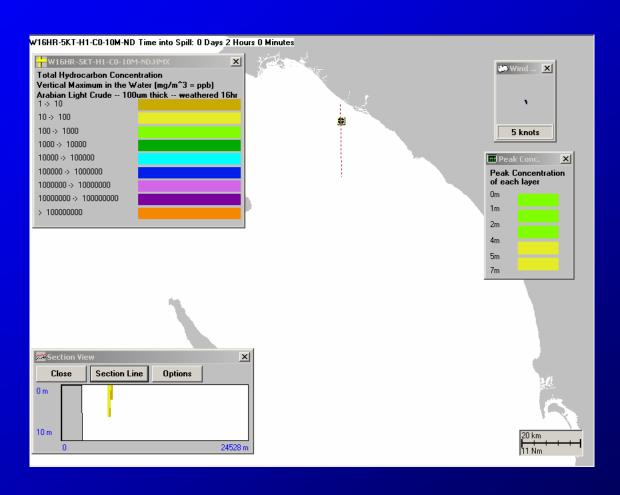


# Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations

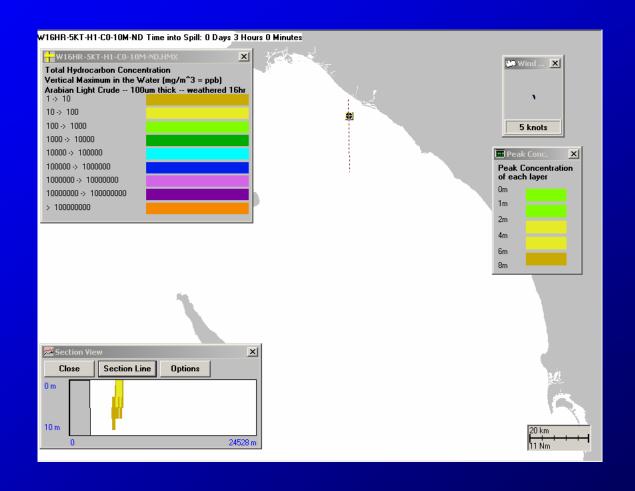
# Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 1 hr after potential treatment



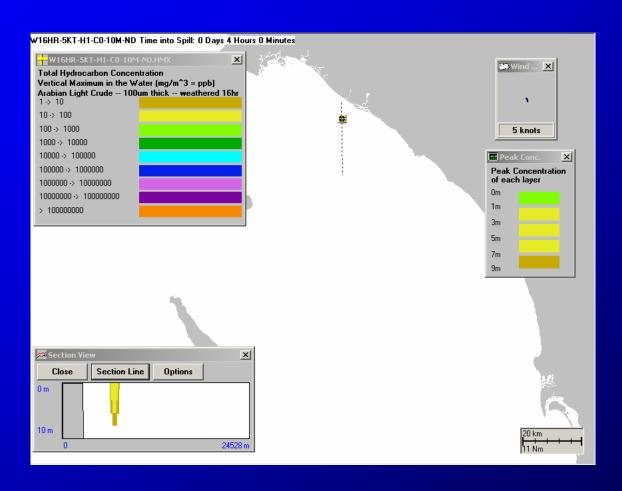
# Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 2 hrs after potential treatment



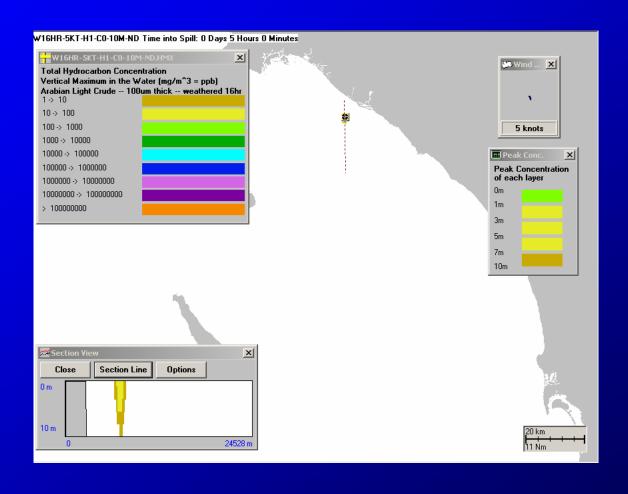
### Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 3 hrs after potential treatment



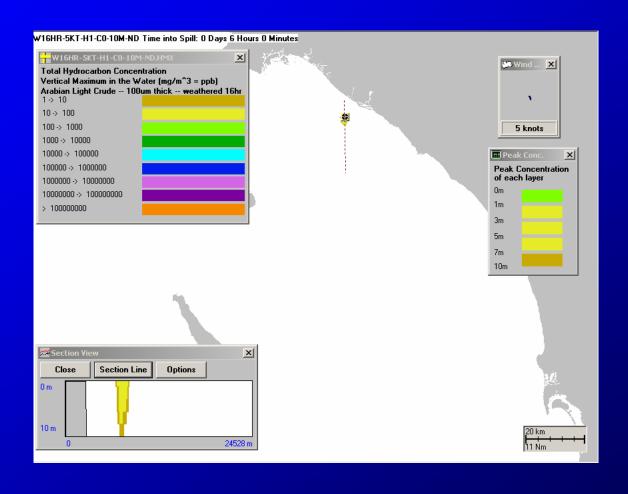
# Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 4 hrs after potential treatment



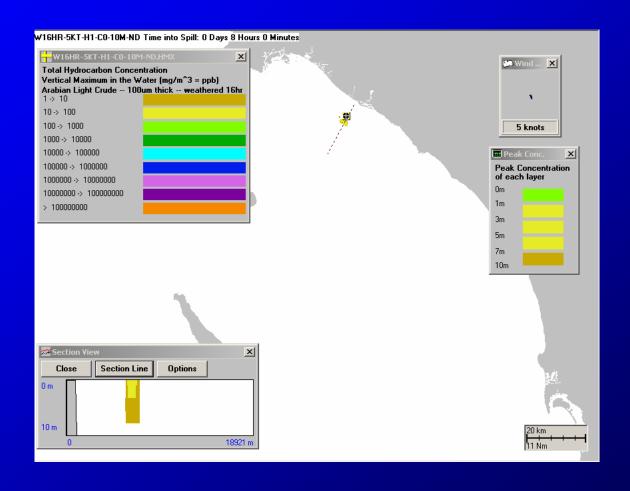
### Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 5 hrs after potential treatment



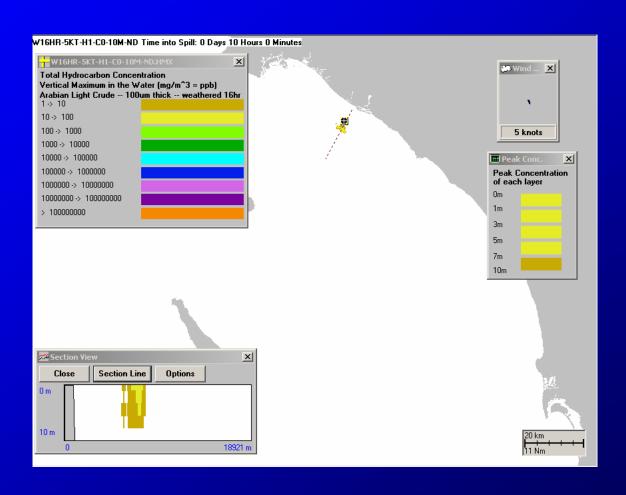
### Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 6 hrs after potential treatment



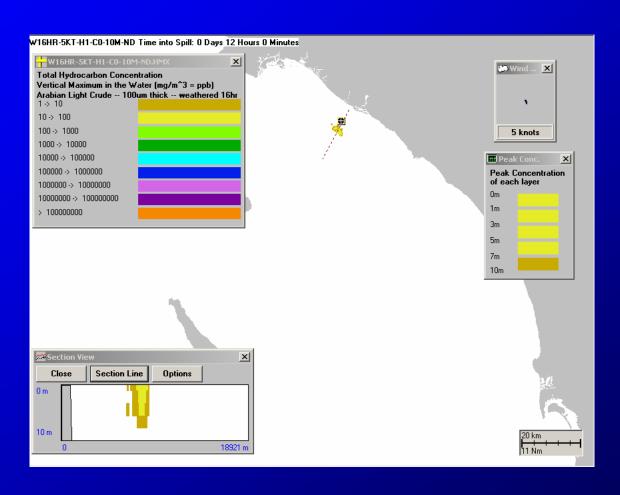
# Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 8 hrs after potential treatment



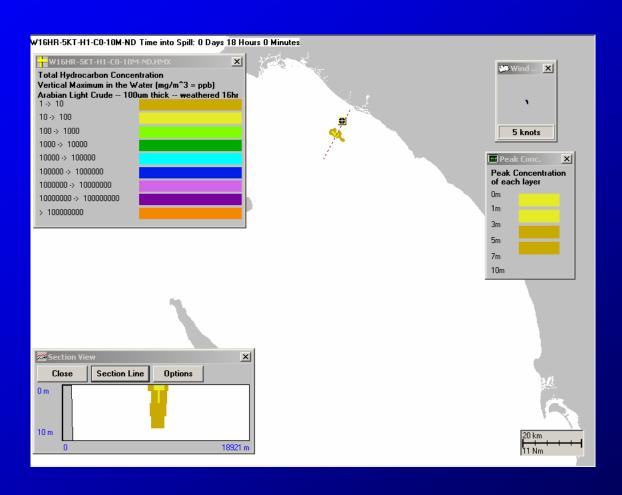
### Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 10 hrs after potential treatment



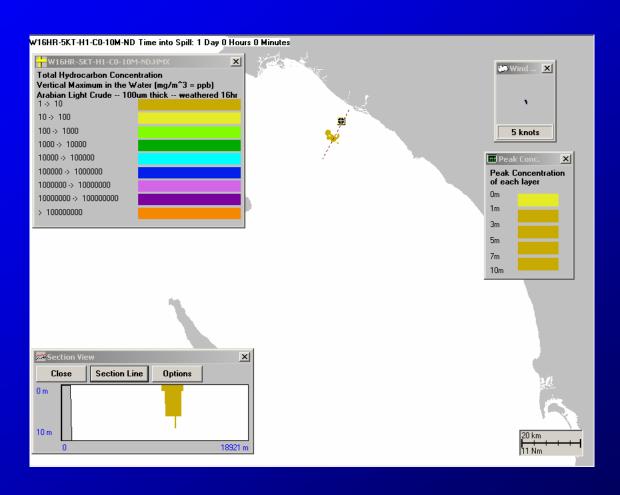
# Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 12 hrs after potential treatment



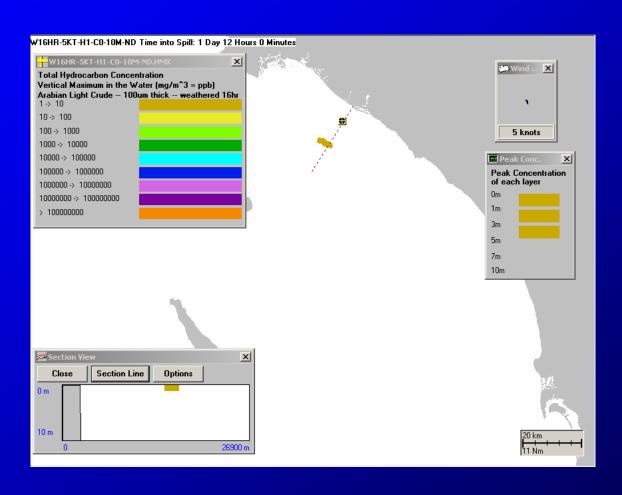
### Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 18 hrs after potential treatment



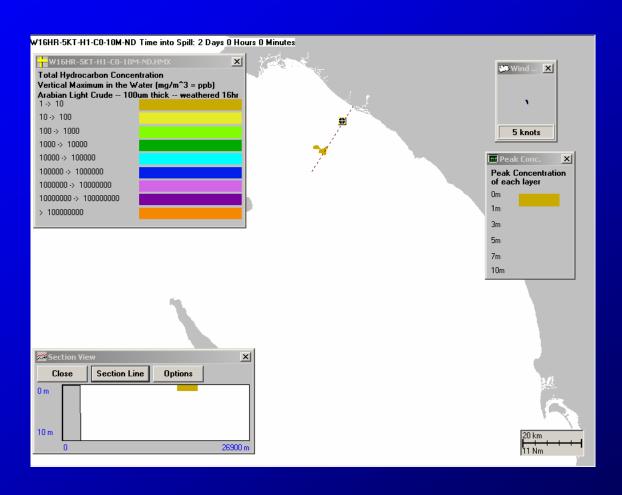
### Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 24 hrs after potential treatment



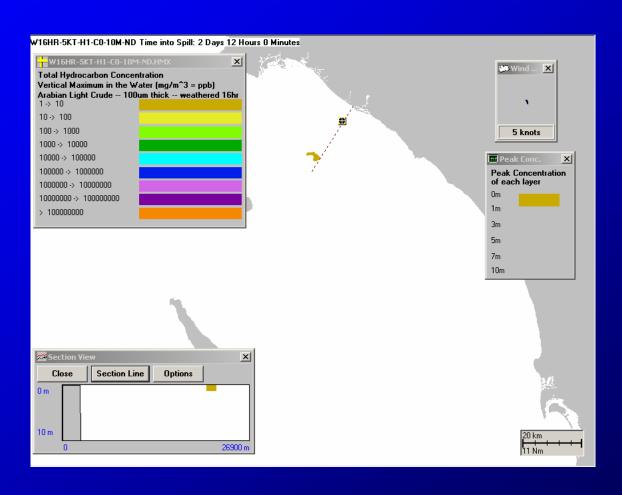
### Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 36 hrs after potential treatment



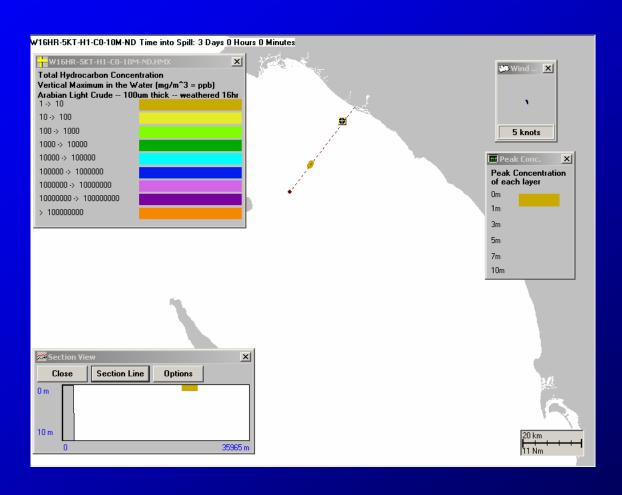
### Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 48 hrs after potential treatment



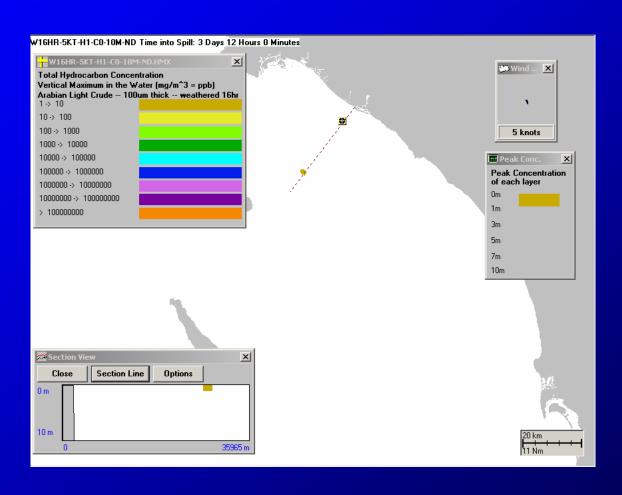
### Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 60 hrs after potential treatment



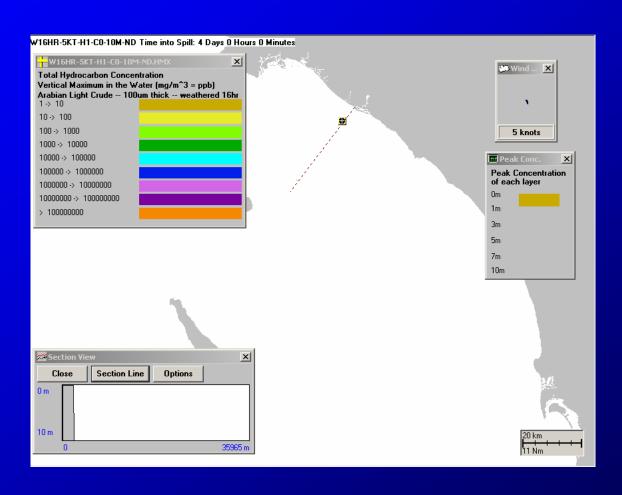
### Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 72 hrs after potential treatment



### Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 84 hrs after potential treatment

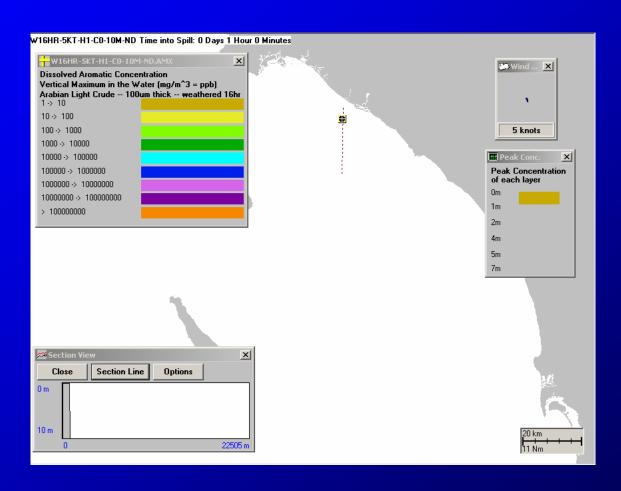


### Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 96 hrs after potential treatment

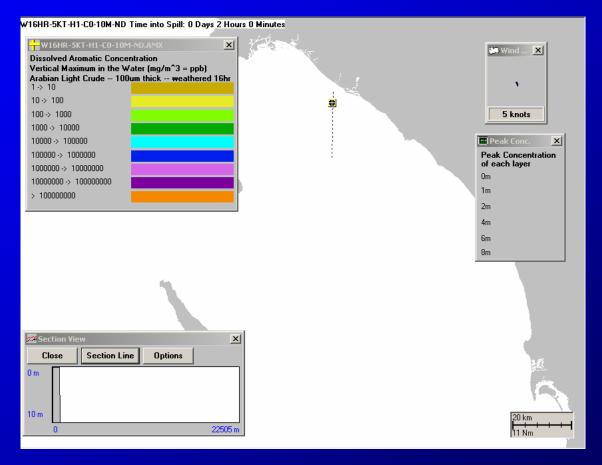


**Dissolved Aromatic Concentrations** 

#### Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Dissolved Aromatic Concentrations: 1 hr after potential treatment



#### Wind from NNW 5 kts; Currents: 0 kt; Dispersant: none; Turbulent mixing to 10m deep; Dissolved Aromatic Concentrations: 2 hrs after potential treatment



\*No dissolved aromatic conc. > 1ppb (averaged) in any grid cell after 2 hrs

#### **Scenario**

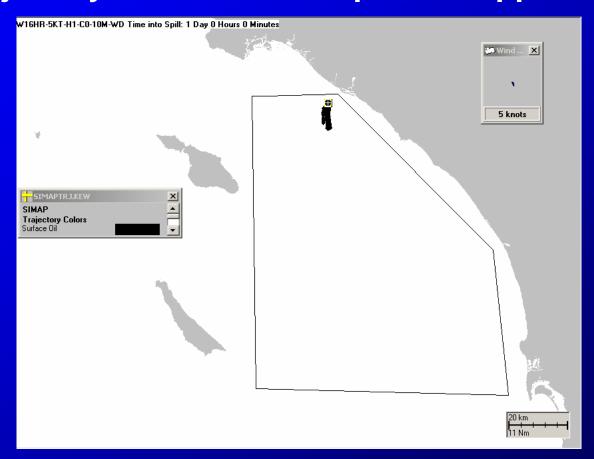
**Pre-Weathering for 16 hrs before dispersant treatment** 

Wind from NNW 5 kts; Currents: 0 kt;

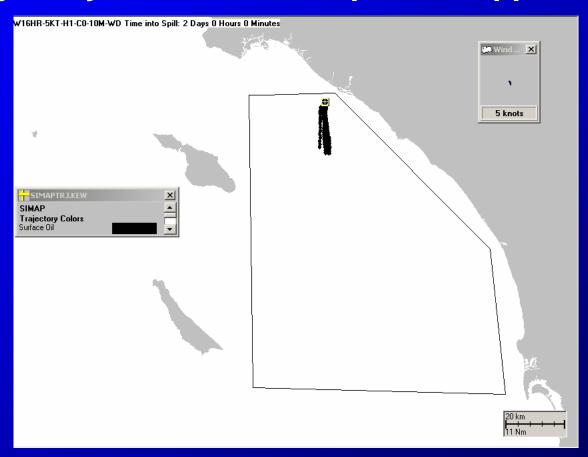
Dispersant: at 16 hrs after Spill

**Turbulent Mixing to 10m deep in Surface Mixed Layer** 

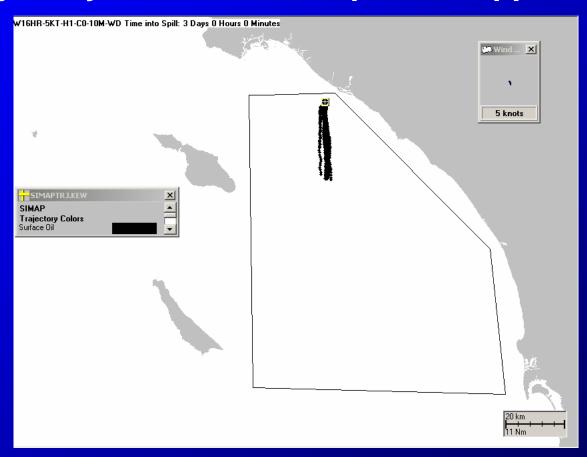
Trajectory: 24 hrs after dispersant application



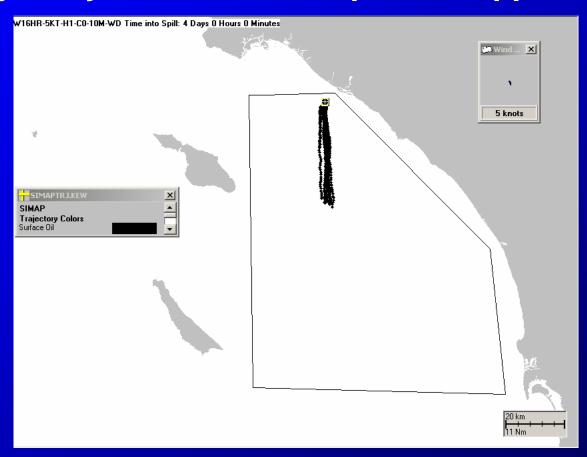
**Trajectory: 48 hrs after dispersant application** 



Trajectory: 72 hrs after dispersant application

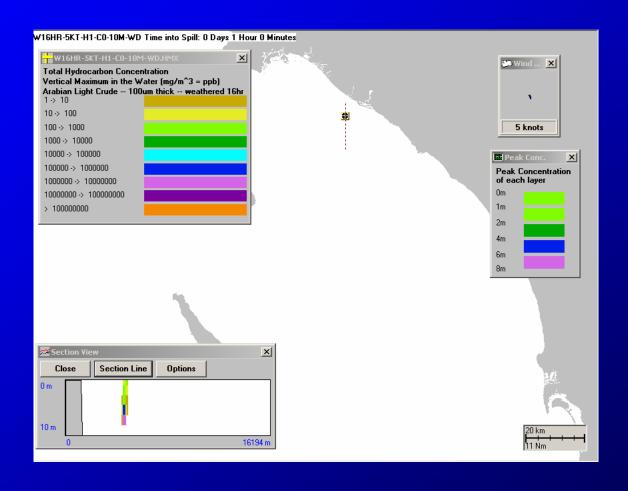


**Trajectory: 96 hrs after dispersant application** 

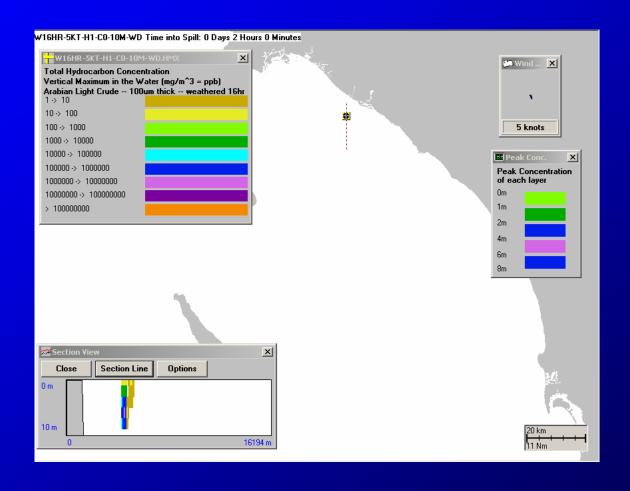


# Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16 hrs; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations

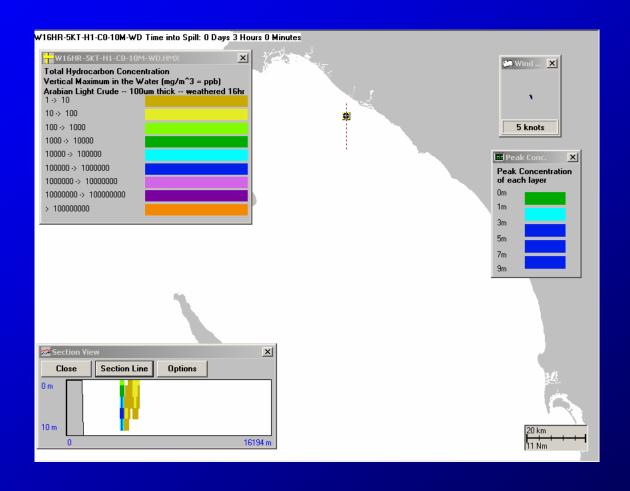
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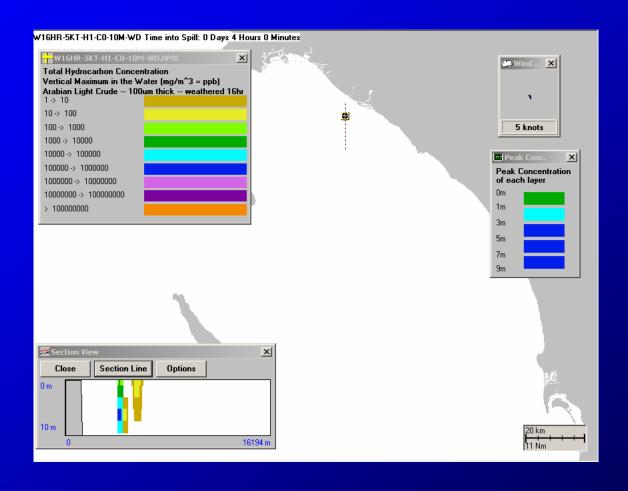
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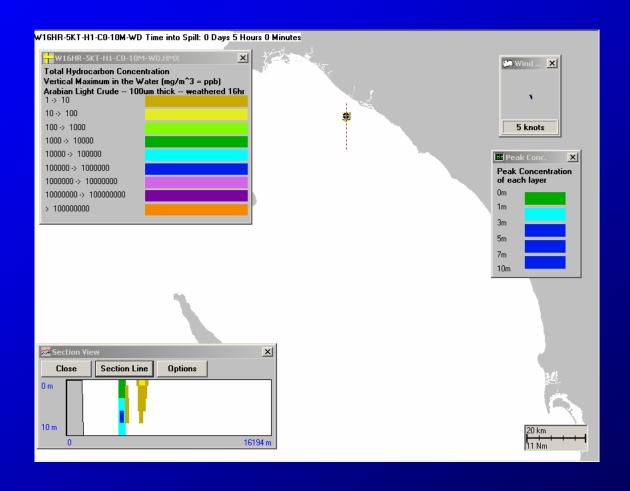
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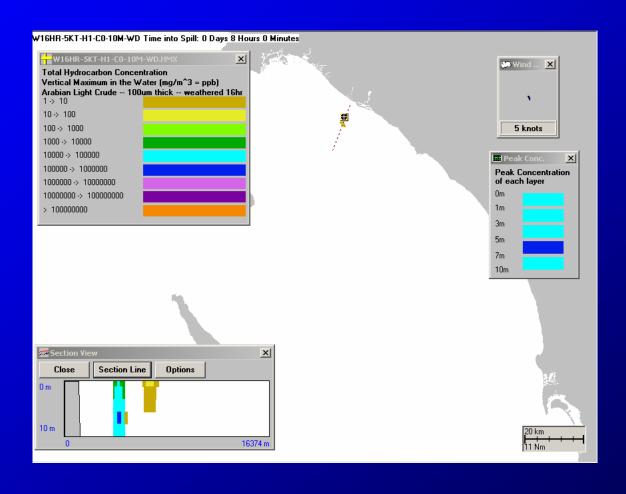
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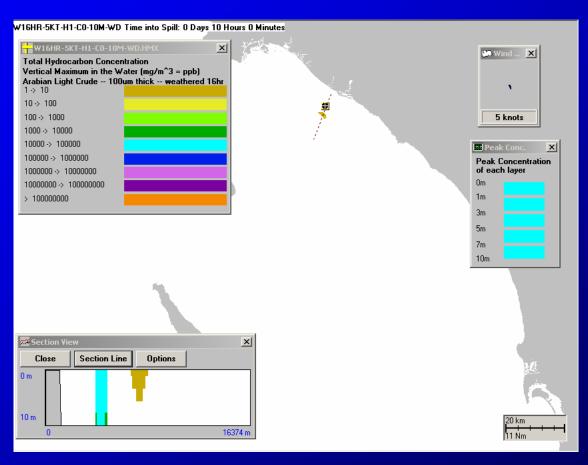
### Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16hrs; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 5 hrs after dispersant application



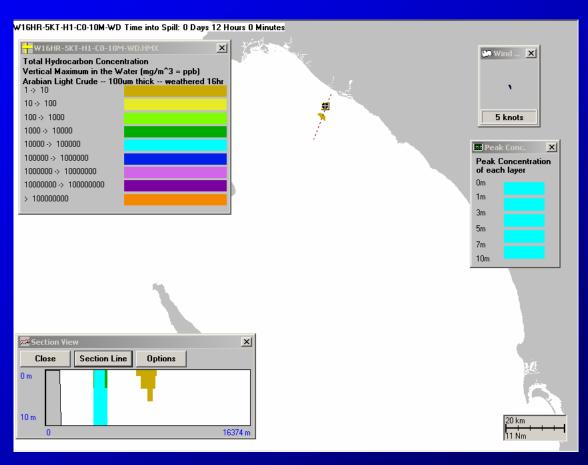
### Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16hrs; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 8 hrs after dispersant application



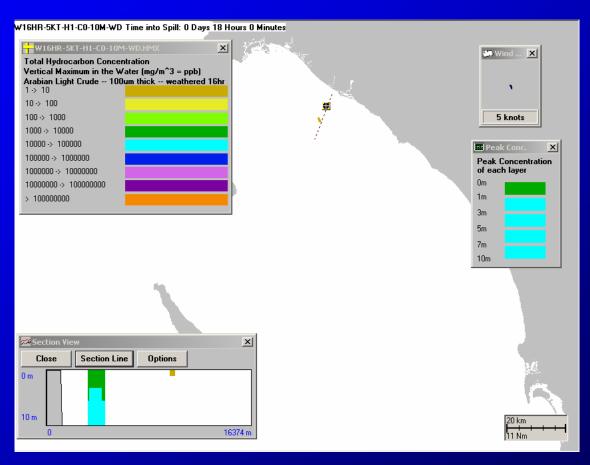
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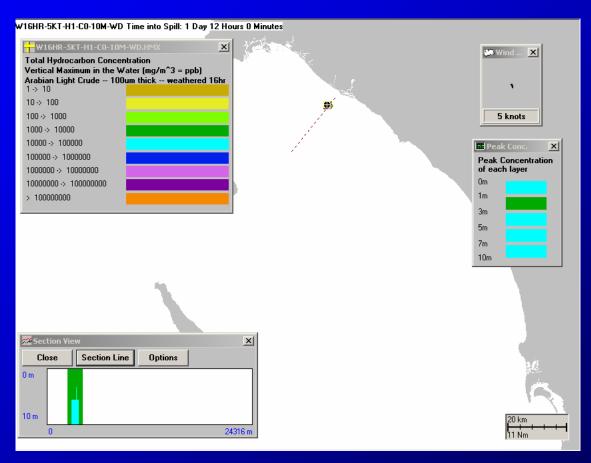
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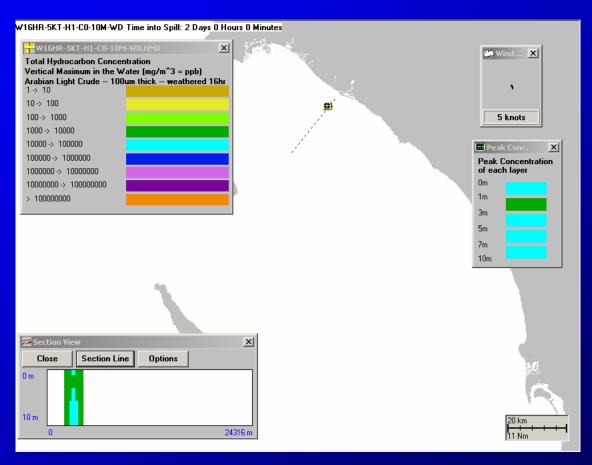
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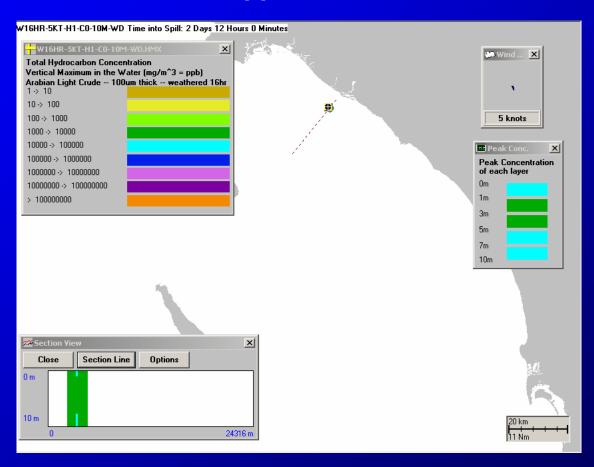
## Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16hrs; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 36 hrs after dispersant application



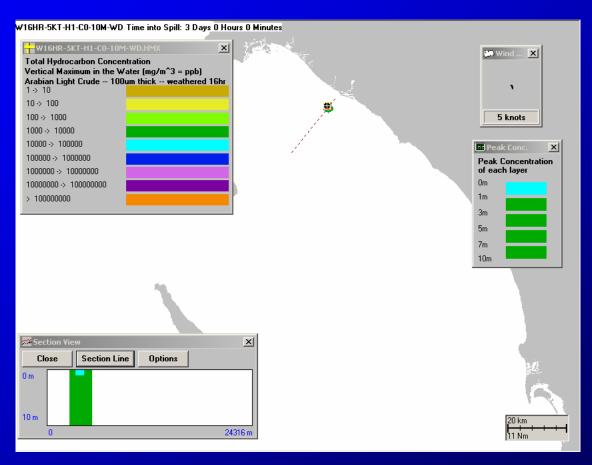
## Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16hrs; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 48 hrs after dispersant application



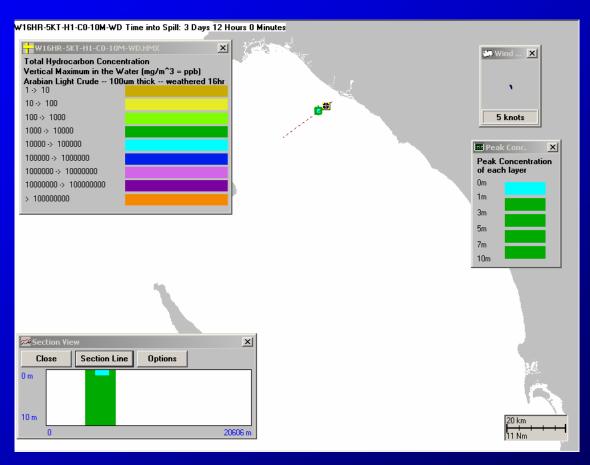
## Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16hrs; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 60 hrs after dispersant application



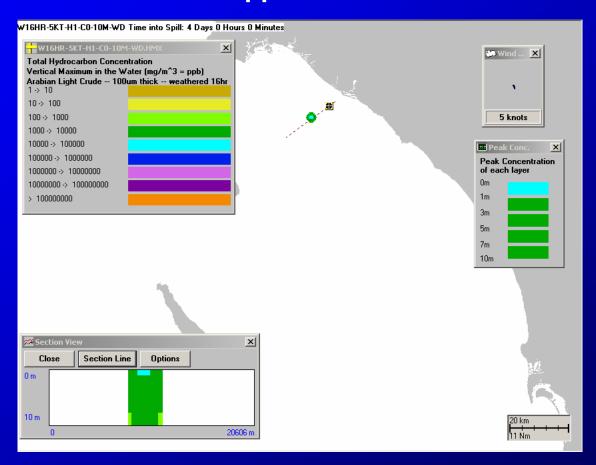
## Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16hrs; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 72 hrs after dispersant application



## Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16hrs; Turbulent mixing to 10m deep; Subsurface Oil Droplet Concentrations: 84 hrs after dispersant application

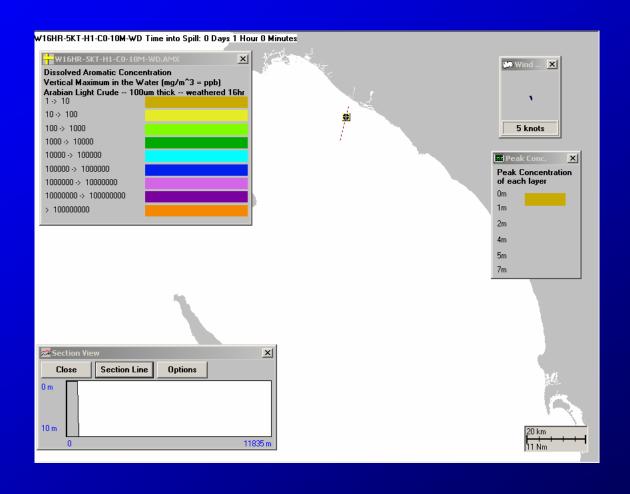


Subsurface Oil Droplet Concentrations: 96 hrs after dispersant application

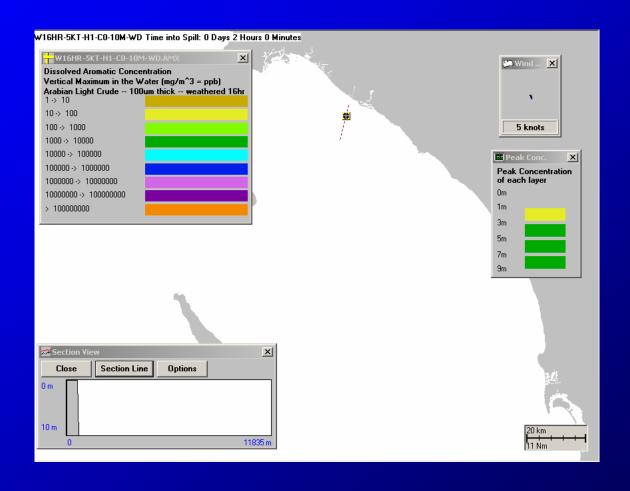


**Dissolved Aromatic Concentrations** 

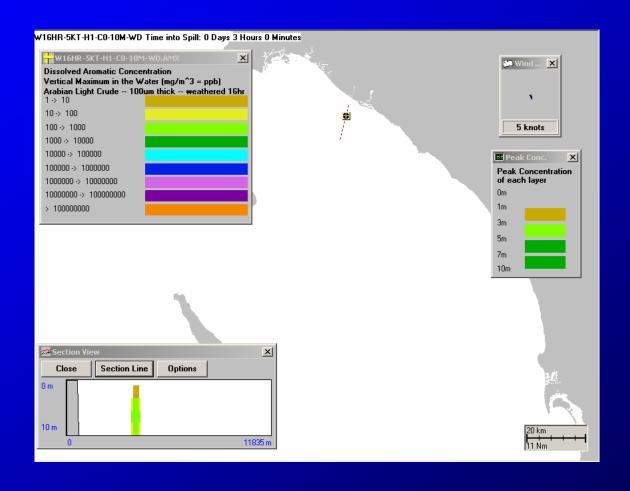
### Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16 hrs; Turbulent mixing to 10m deep; Dissolved Aromatic Concentrations: 1 hr after dispersant application



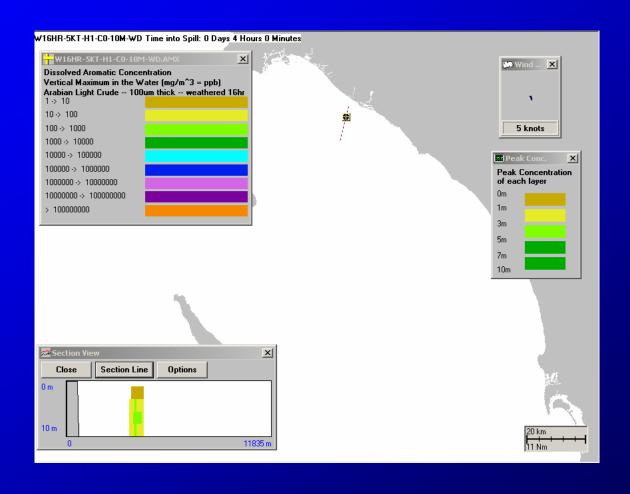
### Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16 hrs; Turbulent mixing to 10m deep; Dissolved Aromatic Concentrations: 2 hrs after dispersant application



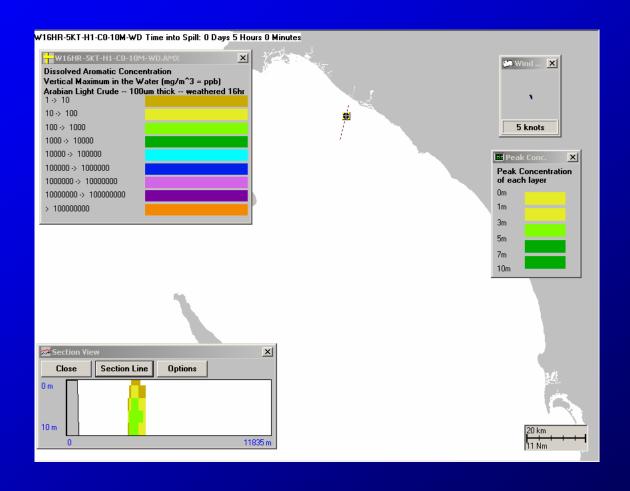
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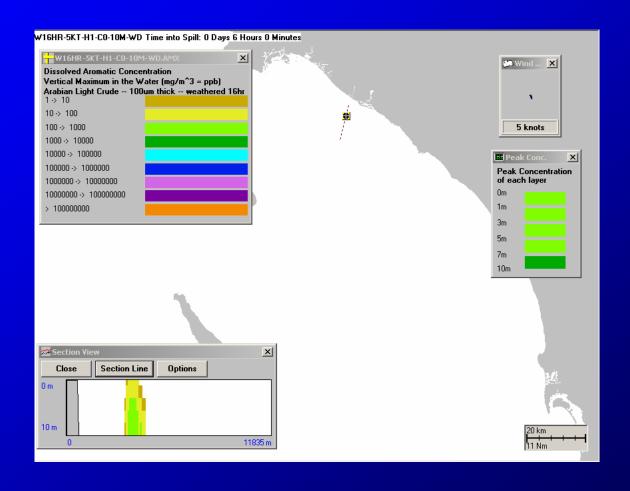
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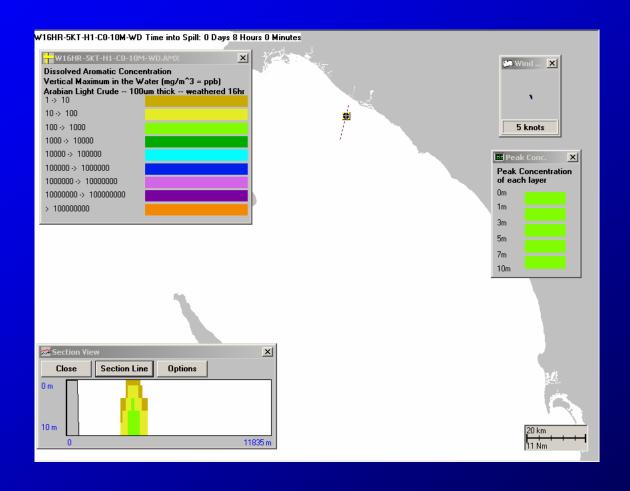
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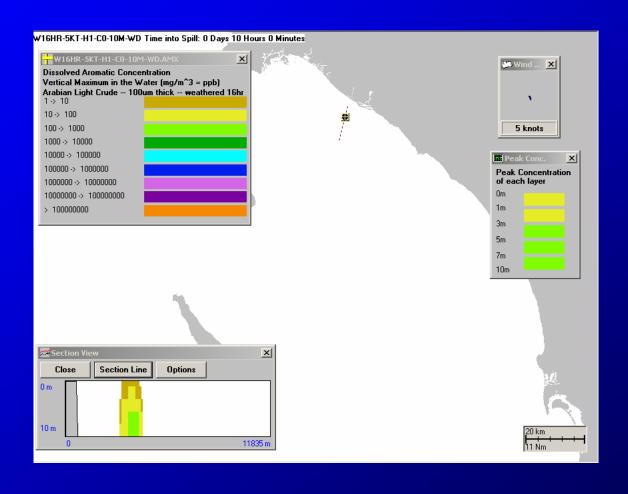
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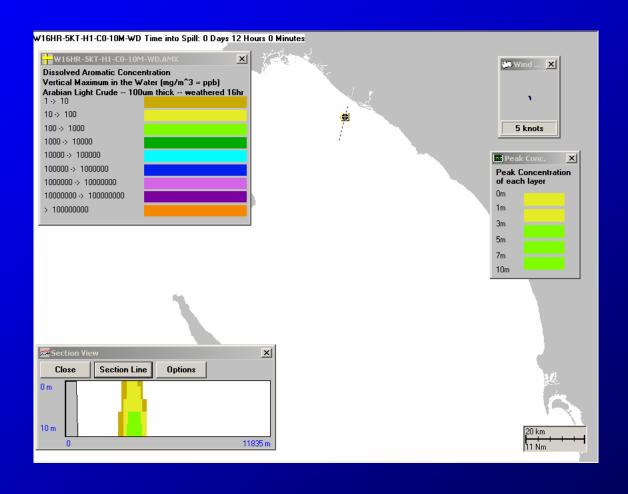
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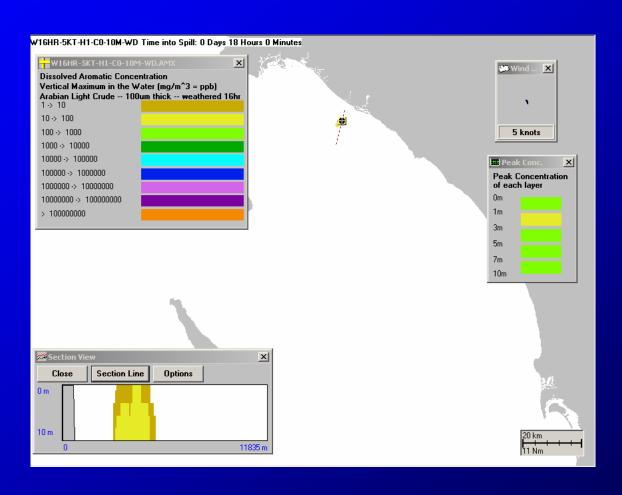
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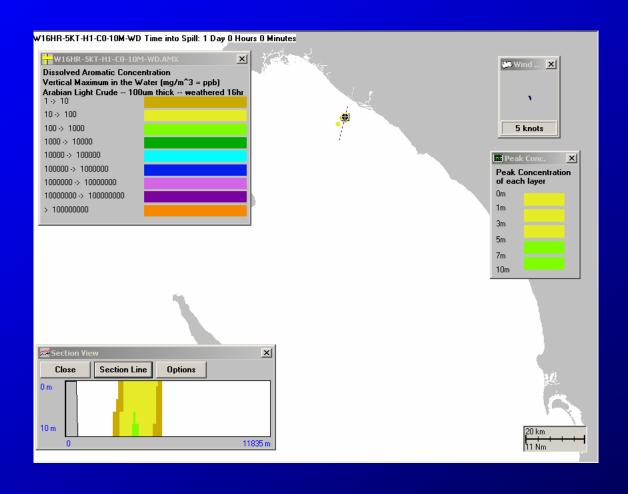
# Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16 hrs; Turbulent mixing to 10m deep; Dissolved Aromatic Concentrations: 12 hrs after dispersant application



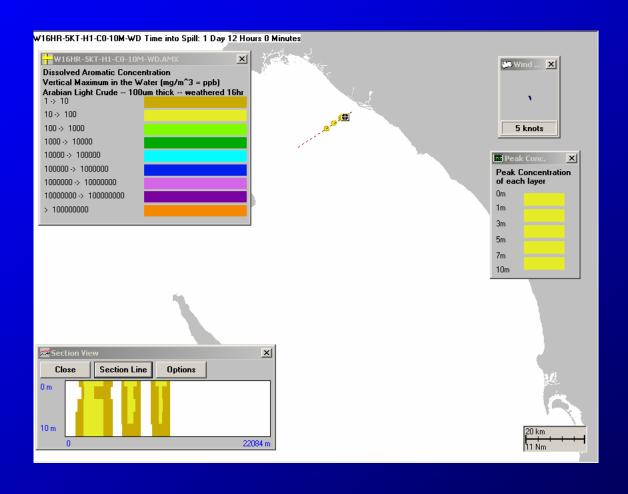
# Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16 hrs; Turbulent mixing to 10m deep; Dissolved Aromatic Concentrations: 18 hrs after dispersant application



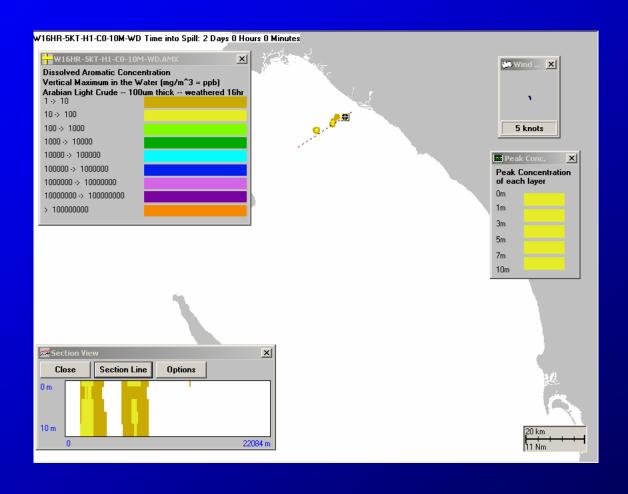
# Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16 hrs; Turbulent mixing to 10m deep; Dissolved Aromatic Concentrations: 24 hrs after dispersant application



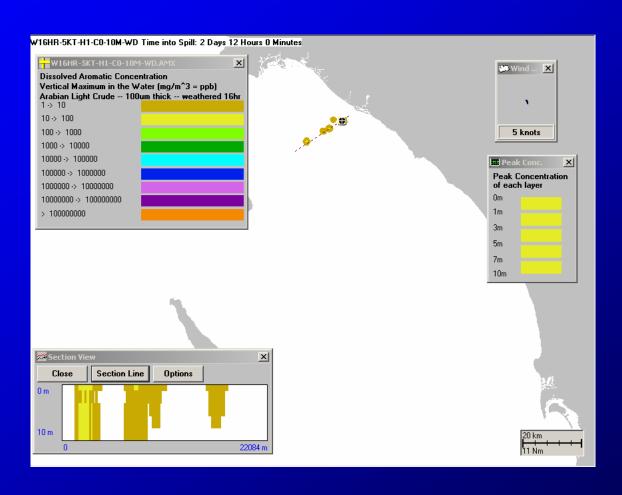
# Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16 hrs; Turbulent mixing to 10m deep; Dissolved Aromatic Concentrations: 36 hrs after dispersant application



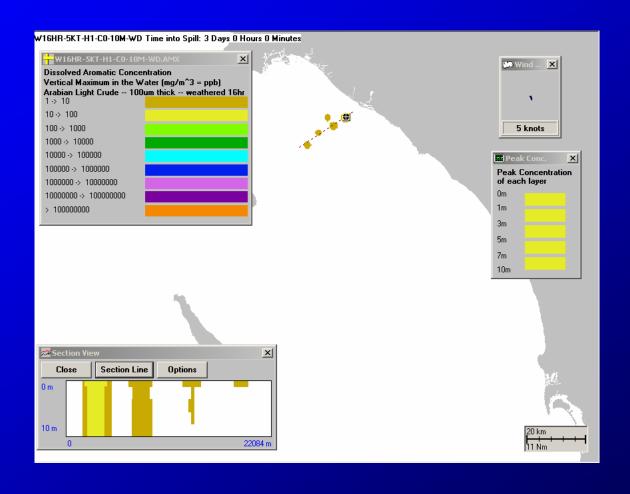
# Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16 hrs; Turbulent mixing to 10m deep; Dissolved Aromatic Concentrations: 48 hrs after dispersant application



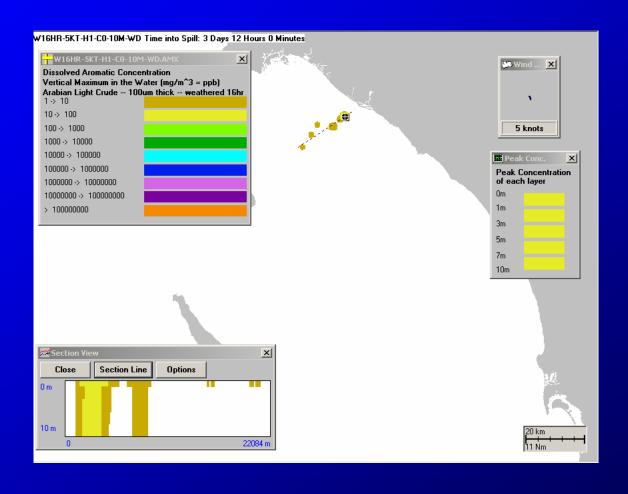
# Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16 hrs; Turbulent mixing to 10m deep; Dissolved Aromatic Concentrations: 60 hrs after dispersant application



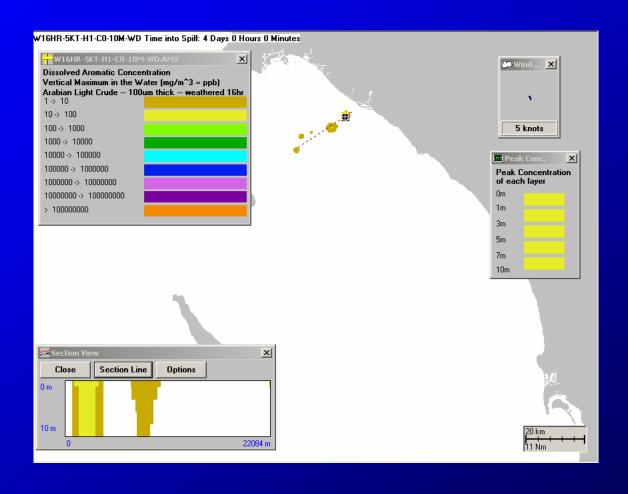
## Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16 hrs; Turbulent mixing to 10m deep; Dissolved Aromatic Concentrations: 72 hrs after dispersant application



# Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16 hrs; Turbulent mixing to 10m deep; Dissolved Aromatic Concentrations: 84 hrs after dispersant application



# Wind from NNW 5 kts; Currents: 0 kt; Dispersant: at 16 hrs; Turbulent mixing to 10m deep; Dissolved Aromatic Concentrations: 96 hrs after dispersant application



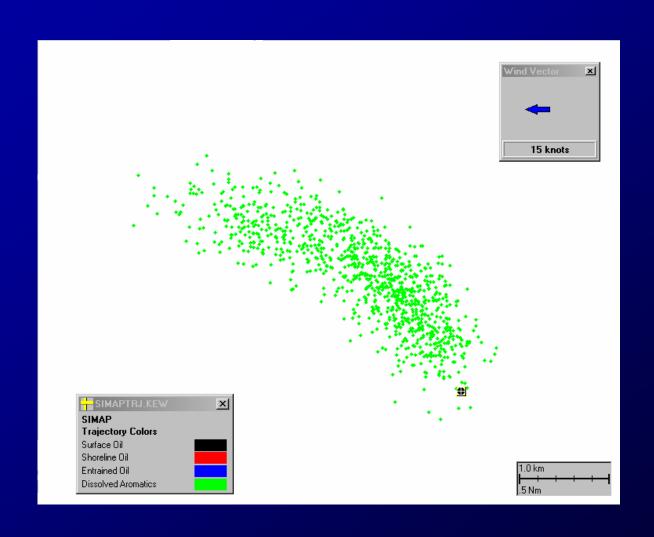
# BIOLOGICAL IMPACT Toxicity Requires Exposure

- Requires Uptake into Organism
  - Some degree of solubility in order for uptake to occur
  - Less soluble components yield lower dissolved concentrations: slower uptake but higher toxicity
- Particulate uptake via gills, organism's surface, or gut
- Concentration that is bio-available
  - Dissolved concentration
  - Small droplets: likely exposure and effects (via dissolved phase)
  - Uptake different for filter-feeders vs. non-filter feeders

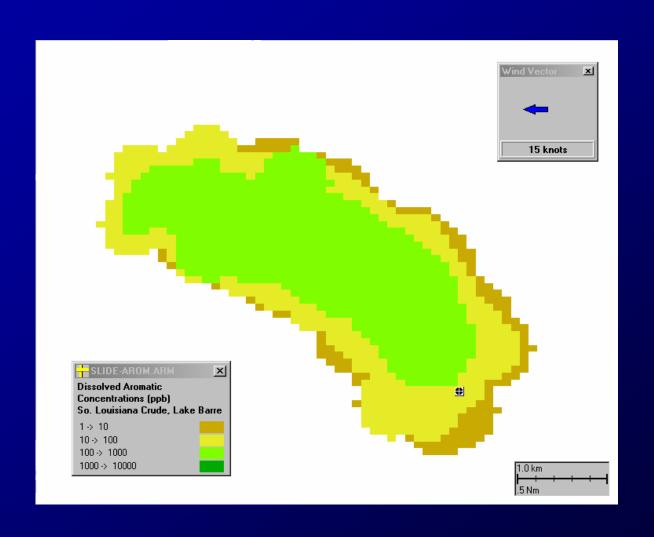
#### Oil Toxicity

- 1-3 ring aromatics cause most of acute toxicity
  - in diesel, heavy fuel, and crude oil, most from PAHs
  - for gasoline, MAHs also
- Dissolved aromatic concentration bioavailable
- Acute and sublethal effects, narcosis

#### **Spillets: Dissolved Aromatics**



#### **Concentration Plume Grid**



#### Biological Exposure Model

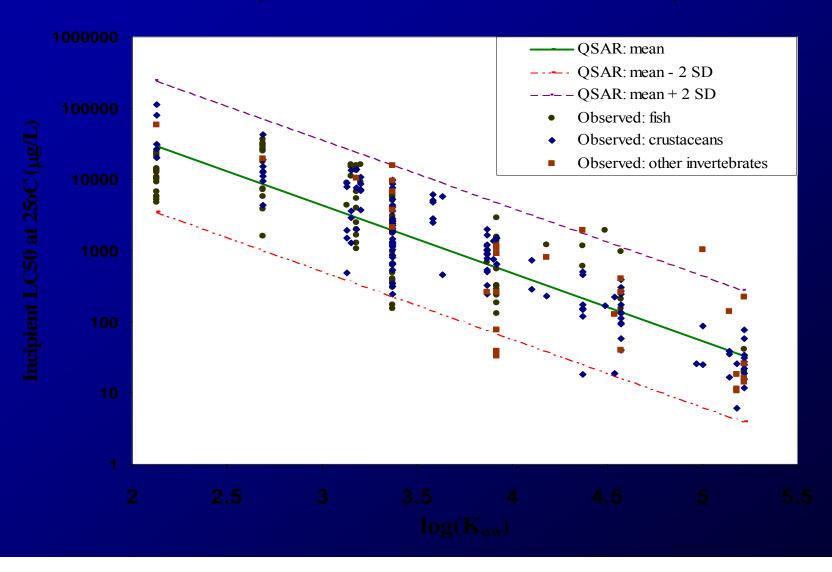
- Organisms classified by behavior
  - Wildlife
    - % of time on water surface
    - Habitats used
    - Feathers & fur
  - Fish and Invertebrates
    - Swimming
    - Drift with currents
    - Stationary
    - Migrations

- Impact a function of dose
  - Wildlife
    - Area swept by oil
    - Oil thickness
  - Fish and Invertebrates
    - Concentration
    - Exposure time
    - Temperature

 Movements of organisms are tracked to calculate exposure of individuals

### Aromatic toxicity – regression of bioassay $LC_{50}$ vs. index of affinity to lipid (log $K_{ow}$ )

Bioassay data from the literature: tests for all species



#### Biological exposure model

Computation LC<sub>50</sub> values for acute toxic effects for 3 sensitivity levels:

- 2.5<sup>th</sup> percentile sensitivity 5 µg/L (ppb) of PAH
- Average sensitivity 50 μg/L (ppb) of PAH
- 97.5<sup>th</sup> percentile sensitivity 400 µg/L of PAH

#### RESULTS

#### **SIMAP Matrix of Runs:**

- 1 location off SoCal
- 1 oil type = light Arabian crude
- 1 spill vol. = max. vol. dispersed by 1 C-130 sortie (100,000 gallons, 80% efficiency, 20:1)
- 1 oil thickness = median value 100µm
- No dispersant use as compared to application after 8 and 16 hours
- 2 wind speeds = 5 kts. and 15 kts.
- 2 mixed layer depth (10 and 20 m)
- 3 current speeds = 0, 0.25 kts. up.- and downwind

#### **RESULTS**

#### Weathering: percent of product remaining

Component	2 hrs. 5kts wind, % left	8 hrs. 5kts wind, % left	16 hrs. 5kts wind, % left
MAHs	85	34	5
2-ring PAHs	99	96	88
3-ring PAH	99	99	97

# **RESULTS**Area impacted > 1 ppb:

No dispersants: 0.05 sq. km = 12 ac.
Volume: 50,000 m<sup>3</sup>

With dispersants: 38 – 108 sq. km
 or 9,400 – 27,000 ac.

Volume: max. 500,000,000 m<sup>3</sup>

#### RESULTS

#### Time of maximum areal impact:

No dispersants: 1 − 13 hours

■ With dispersants: 20 – 200 hours

#### RESULTS

#### **Acute toxicity and potential impacts:**

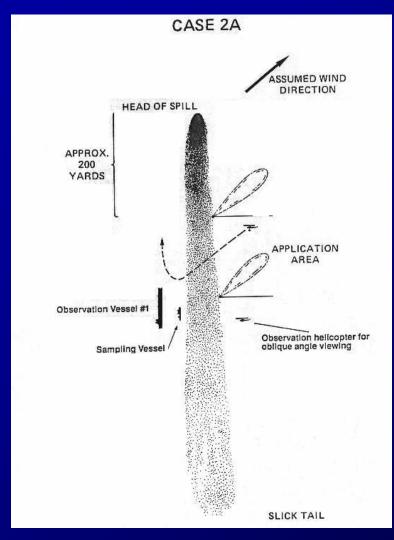
- Sensitive species: < 19 sq. km = 4,700 ac. (5 ppb PAH)</p>
- Average species: < 2 sq. km = 500 ac. (50 ppb PAH)
- Robust species: <0.05 sq. km = 12 ac. (400 ppb PAH)

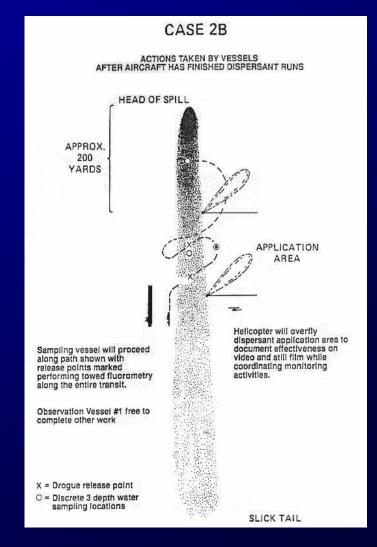
#### FIELD IMPLEMENTATION OF DOMP

#### **Important measurements:**

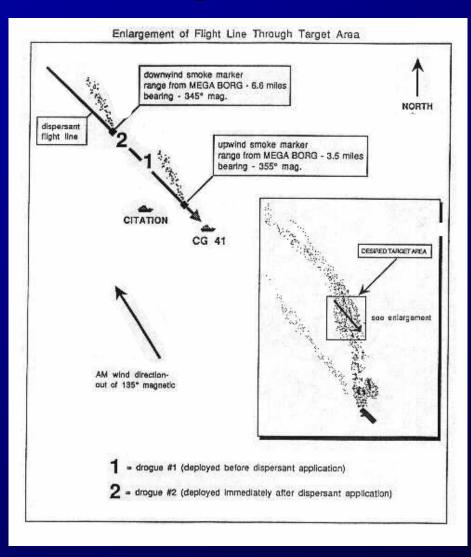
- Near-surface currents (Drogues, CODAR ?)
- Continuous sub-surface plume tracking using SIO towed UV/Fluorometer
- Water samples (Go-Flo bottles & PLVWSS)
- Mixed layer depth (CTD casts)
- Wind speed and direction (direct observation)
- Zooplankton species composition (net tows)

# Approaches to Field Sampling for Impact Monitoring (from Payne et al. 1991)

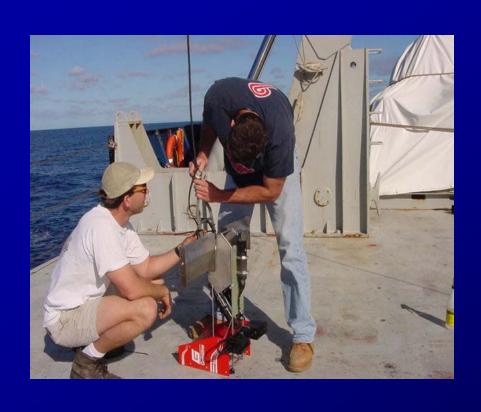




# Approaches to Field Sampling for Impact Monitoring (from Payne et al. 1993)

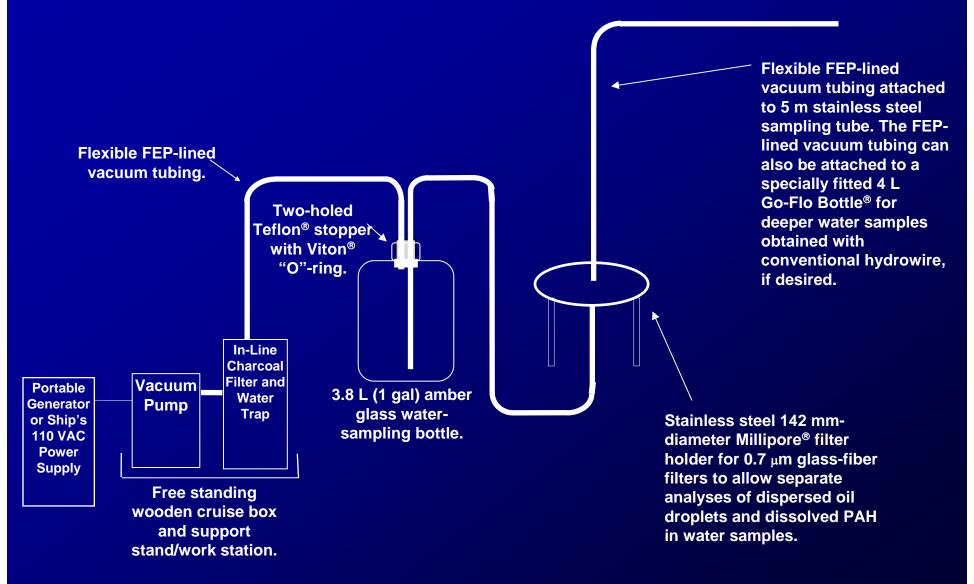


# SIO Towed UV/Fluorometer for Plume Definition and Tracking



- Towed at fixed & variable depths
- Real-time signal fed back to surface vessel
- Towing speeds of 2-15 knots allow rapid measurements
- Minimum plume disturbance

### Schematic diagram of the Portable Large-Volume Water Sampling System (PLVWSS)



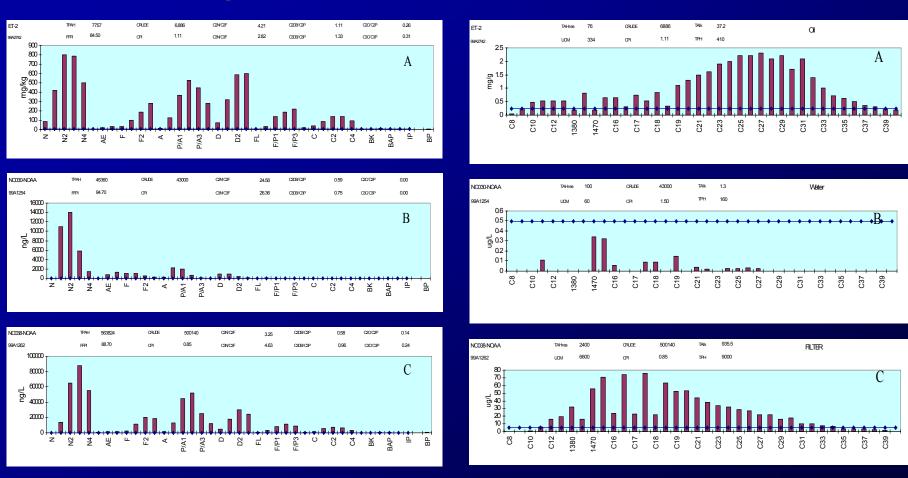


Offshore near-surface and near-bottom water sampling using the PLVWSS and a conventional Go-Flo Bottle® from a chartered vessel-of-opportunity during the *M/V New Carissa* oil spill off of Coos Bay, Oregon. February 1999.



Offshore processing of near-surface and near-bottom water samples collected with a conventional Go-Flo Bottle® during the *M/V New Carissa* oil spill. The sample is pumped directly from the Go-Flo Bottle® into the PLVWSS for separation of dissolved and particulate/oil droplet fractions.

# PAH and SHC Oil Components Measured During the *M/V New Carissa* Spill



PAH Components (mg/Kg and ng/L)

SHC Components (mg/g and  $\mu$ g/L)

(A) Beached Oil; (B) Dissolved Components; & (C) Physically Dispersed Oil Droplets

#### Plankton and Neuston Sampling





Oblique "Bongo" net tows sample the water column.

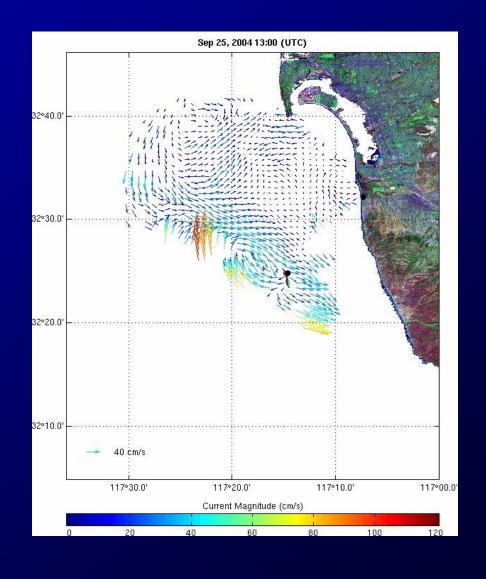
The floating "Manta" net collects surface samples.

#### Plankton Exposure Assessment

- Don't sample in oil slick or dispersed oil plume.
- Sample in uncontaminated adjacent waters for documentation of species and age-group composition.
- Complete separate tows for collection of live zooplankton and egg samples for later laboratory toxicity studies at field-observed PAH and oil-droplet concentrations.
- Can be completed during or following the emergency phase of field operations.

#### FIELD VALIDATION OF DOMP

- OSPR-funded shakedown cruises to validate DOMP sampling approach.
- Simulated dispersed oil plume (fluorescein dye).
- Integration of SIMAP and Coastal Ocean Dynamic Applications Radar (CODAR).



#### **CONCLUDING THOUGHTS**

- Patchy distribution of dispersed oil droplets and dissolved components complicates sampling.
- DOMP approach is based on experience from Pac Baroness and Mega Borg spill-of-opportunity studies.
- Plume sampling would be impossible without subsurface drogues and real-time UV/Fluorescence measurements.
- PLVWSS allows assessment of dissolved PAH vs. oildroplets and direct comparison to SIMAP predictions.
- Biological injury assessment for zooplankton and eggs drifting with dispersed oil plume (potential longer duration exposure).
- Testing field approach with shake-down cruises and dye studies.

#### Questions?



#### Thank you!





